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A high-power pulsed tunable dye laser system was acquired in order to carry out a variety of spectroscopic studies of the weak, non-bonding interactions of light atoms, such as boron and carbon, with hydrogen and other species.

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FY94 DURIP WEAK INTERACTIONS INVOLVING LIGHT ATOMS

FINAL REPORT

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ITEMIZATION OF EQUIPMENT PURCHASED

The funds awarded under grant no. F49620-95-1-0057 were used to acquire a Nd:YAG laser pumped dye laser system capable of producing relatively high-power narrow-band laser radiation from the ultraviolet to the near infrared.

The following specific items were purchased under this grant:

A.   Nd:YAG laser pumped dye laser system

     Vendor: Continuum, Santa Clara, CA.

(1) Model Powerlite 8010 Q-switched Nd:YAG laser system, 10 Hz

(2) DS, TS temperature stabilized second and third harmonic generators

(3) WSP-2 wavelength separation package for second and third harmonic outputs

(4) SI-500 injection seeder for SLM operation

(5) ND6000 high-energy nanosecond dye laser for Nd:YAG pump laser (includes NBP narrow bandwidth package)

(6) DGO-1 dual grating option for ultra-narrow linewidth over 510-715 nm

(7) UVG ultraviolet grating

(8) DGO-3 dual grating option for ultra-narrow linewidth over 415-570 nm

(9) UVX-1 components for frequency doubling output of dye laser

(10) UVT-1 closed loop crystal tracking for UVX-1

(11) DCC-4 frequency doubling crystal, range 220-260 nm

(12) DCC-3 frequency doubling crystal, range 267-295 nm

(13) DCC-2 frequency doubling crystal, range 295-365 nm

B.   Gated integrator

     Vendor: Stanford Research Systems, Sunnyvale, CA.

(1) SR250 gated integrator

The equipment purchased differs slightly from the list itemized in the proposal. Specifically, a delay generator was not purchased. Instead, the Nd:YAG laser was equipped with an injection seeder for single longitudinal mode operation. This change was made on the basis of consultations with Continuum engineers and several chemical physics colleagues. The line profile from a dye laser pumped with an unseeded Nd:YAG laser has been found to have a pedestal, above which is the sharp central portion of the profile. If the dye laser were used for non-linear optical generation, for example in vuv generation by frequency tripling in a gas, then the pedestal in the visible dye laser profile would cause a significant frequency broadening of the vuv output. Use of a seeded Nd:YAG laser as the pump would eliminate the pedestal and keep the vuv linewidth small.

SUMMARY OF RESEARCH ACCOMPLISHED

The equipment acquired under grant no. F49620-95-1-0057 is being used in the following projects:

1. Radiative and nonradiative decay of electronically NCO

Before integrating this laser system into AFOSR-supported work, we chose to break in this laser system on a relatively instrumentally undemanding project. The use of the laser system for this project also allowed my group to become familiar with the intricacies of alignment and maintenance of the system. It turned out that we encountered a number of problems with the system, and these were worked out during the course of this initial project. Problems encountered included rapid burning of dye cuvettes (from contamination in the dye circulation system), a miswired computer interface cables, several bad dc power supply boards. Since these systems have been fixed by Continuum, the laser system has been operating reasonably reliably.

The initial problem for which the laser system was employed was the study of the decay of electronically excited NCO radicals. This radical appears to be an important intermediate in the combustion of nitrogen-rich fuels[1] and in the decomposition of nitramines,[2] and laser fluorescence detection offers a convenient and sensitive method for its detection. There are two low-lying excited electronic states of NCO, $\tilde{A}\,^2\Sigma^+$ and $\tilde{B}\,^2\Pi$, whose origins are 22,800 and 31,750 cm^{-1}, respectively, above the $\tilde{X}\,^2\Pi$ ground state. All the vibrational levels of the excited electronic states lie above lowest, spin-forbidden dissociation asymptote, $N(^4S) + CO(X\,^1\Sigma^+)$. Neumark and co-workers[3] have studied the photodissociation of NCO in a fast beam experiment. They find that all vibrational levels of the $\tilde{B}\,^2\Pi$ state are dissociative, even below the onset of the spin-allowed $N(^2D) + CO(X\,^1\Sigma^+)$ dissociation channel. The radiative lifetime of the $\tilde{A}\,^2\Sigma^+$ zero-point vibrational level has been measured to be ~ 400 ns,[4] and there is no evidence for predissociation of the lower levels of the $\tilde{A}\,^2\Sigma^+$ state.

Alexander and Werner[5] have carried out electronic structure calculations to understand more fully the mechanism of the dissociation of the NCO $\tilde{B}\,^2\Pi$ state. They find that this process occurs through an indirect mechanism,[6] in which the $\tilde{B}\,^2\Pi$ state is crossed

3

by the lower-lying $\tilde{A}\,^2\Sigma^+$ state, which is, in turn, crossed by a repulsive $^4A''$ state which correlates with the ground state asymptote, $N(^4S) + CO(X\,^1\Sigma^+)$. The crossing of the $\tilde{A}$ and $\tilde{B}$ states occurs near the equilibrium geometry of the latter state, and at an energy only slightly higher than its minimum energy. These calculations hence provide an explanation for the $\tilde{B} \sim \tilde{A}$ perturbations observed by Dixon and co-workers[7, 8] in the $\tilde{B} - \tilde{X}$ band system. The calculations of Alexander suggest that high vibrational levels of the $\tilde{A}\,^2\Sigma^+$ state should also be predissociated by coupling with the $^4A''$ state. The $\tilde{A} - {}^4A''$ crossing is predicted to occur at an energy only slightly below that of the minimum of the $\tilde{B}$ state, in a bent nuclear geometry.

We have measured decay lifetimes of electronically excited NCO in order to characterize the higher vibrational levels in the $\tilde{A}\,^2\Sigma^+$ state and to observe the onset of predissociation in NCO. Presently, the highest directly identified level in the $\tilde{A}$ state[9] lies $\sim 3,700$ cm^{-1} below the energy of the $\tilde{B}$ state. As our source of NCO, we have employed the $CN + O_2$ reaction, for which we have carried out several studies of the reaction dynamics through photolysis of a CN precursor and laser fluorescence detection of the NCO product as a function of the photolysis-probe delay in a slowly flowing gas mixture.[10, 11]

We have newly observed a number of $\tilde{A}\,^2\Sigma^+$ vibrational levels and have been able to make assignments to many of these. Decay lifetimes for $NCO(\tilde{A}\,^2\Sigma^+, \tilde{B}\,^2\Pi)$ levels were measured for excitation energies over the range $27,000 - 33,000$ cm^{-1}. Up to $\sim 30,000$ cm^{-1}, the lifetimes did not vary greatly and fell in the range $240 - 310$ ns. These values are somewhat lower than for the $NCO(\tilde{A})$ zero-point level but are consistent with the expected slight falloff of an excited state radiative lifetime with increasing vibrational energy because of the ν^3 factor in the spontaneous emission rate. Unfortunately, levels with excitation energies between $28,000$ and $31,500$ cm^{-1} could not be studied since their band strengths were too weak. Just above this energy is the zero-point level of the $\tilde{B}\,^2\Pi$ state. We find a wide variation of the lifetime for excitation of different rotational levels within this vibronic level. Above the $\tilde{B} - \tilde{X}$ origin band, the measured lifetimes drop rapidly with increasing excitation energy to values ≤ 10 ns.

Our observations of NCO decay lifetimes are consistent with the calculations of Alexander and Werner,[5] who predicted that the onset of predissociation should be near the

energy of the ground vibrational level of NCO($\tilde{B}\,^2\Pi$). This work is now being written up for publication.

2. Fluorescence depletion spectroscopy of boron van der Waals complexes

Since this laser system was installed in our laboratory, our main effort has been its use of observe non-fluorescing excited electronic states of van der Waals complexes of the boron atom with Ne, Ar, and H_2. In our ongoing AFOSR-supported project funded through grant no. F49620-95-1-0055, we have been carrying out spectroscopic studies to characterize the non-bonding interactions of the boron atom, and other light atoms.

In these experiments, we prepare complexes of the B atom in a free-jet expansion, through 193 nm photolysis of a small amount of diborane (~ 0.5%) added to the beam seed gas mixture. Boron atoms and complexes are detected downstream by laser fluorescence excitation in the wavelength range around B atomic transitions. These are two allowed B atomic transitions for wavelengths > 200 nm, namely the $2s^23s\,^2S \leftarrow 2s^22p\,^2P$ transition at 249.8 nm and the $2s2p^2\,^2D \leftarrow 2s^22p\,^2P$ transition at 208.9 nm. In previous experiments, we have observed the electronic spectrum of the BAr,[12-14] BNe,[15] and B$\cdots$H$_2$[16] complexes built upon the $3s \leftarrow 2p$ atomic transition and have used these observations to help characterize the relevant interaction potentials of the ground and excited B atoms with these species, in conjunction with collaborative theoretical calculations by Alexander and co-workers.[12, 13, 15, 17] The interaction energies involving the ground electronic states have weak binding energies, while the excited potentials display an extremely varied behavior. The BAr($B^2\Sigma^+$) state have a deep well with a barrier to dissociation. By contrast, the BNe($B^2\Sigma^+$) and B($3s$)$\cdots$H$_2$ interaction potentials are purely repulsive.

In recent experiments, we have observed in laser fluorescence excitation experiments several BNe electronic states correlating with the higher B($2s2p^2\,^2D$) atomic asymptote.[18] This atomic state differs significantly from the lower state in that it is an excited *valence*, rather than Rydberg, state. There are three molecular electronic states, of Δ, Π, Σ^+ symmetry, which emanate from this asymptote. We have observed resolved bands corresponding to excitation of several vibrational levels of the BNe $C^2\Delta$ and $D^2\Pi$ states. The binding energy of the $C^2\Delta$ state was found to be somewhat larger than that of the

ground $X^2\Pi$ state, while the $D^2\Pi$ state is only weakly bound. The $^2\Sigma^+$ state is expected to be repulsive and was not positively identified in the spectrum.

We have searched for the corresponding higher excited states of the BAr, BKr, and B$\cdots$H$_2$ complexes. For BAr and BKr, transitions to bound vibrational levels were observed in the wavelength region around the B atomic $2s2p^2\ ^2D \leftarrow 2s^22p\ ^2P$ transition. However, the derived binding energies of the observed excited electronic states was much less than for BNe($C^2\Delta$), which did not seem reasonable. We also searched, unsuccessfully, for laser fluorescence excitation of the B$\cdots$H$_2$ complex in this wavelength range.

To augment our search for electronic transitions of these complexes, we have implemented a fluorescence depletion technique, which allows the observation of a non-emitting state through tagging via another, fluorescing excited state. In this spectroscopic method, which requires three lasers for our application (photolysis laser, depletion and probe lasers), the probe laser is tuned to excite fluorescence from the complex whose spectroscopy we wish to pursue further. The depletion laser is spatially overlapped with the probe laser but is slightly advanced in time. The fluorescence depletion spectrum is obtained by tuning the depletion laser. If this laser should excite the complex, then the probe laser induced fluorescence signal will drop because of a decrease in the concentration of the complex.

As a test of this technique, we mapped out the spectrum of BNe around the B atomic $2s2p^2\ ^2D \leftarrow 2s^22p\ ^2P$ transition with the probe laser tuned to the maximum of the $B-X$ free $\leftarrow$ bound transition. The depletion spectrum mapped out the corresponding fluorescence excitation spectrum, but with a decreased signal-to-noise ratio, since the depletion spectrum must be taken as the difference of two non-zero signals.

We have used this technique to investigate further the spectra of BAr and B$\cdots$H$_2$ in the vicinity of the B atomic $2s2p^2\ ^2D \leftarrow 2s^22p\ ^2P$ transition. For BAr, we observed two electronic transitions in this wavelength range. The less strongly bound excited state was previously observed in the laser fluorescence excitation spectrum and is assigned as the $D^2\Pi$ state. The more strongly bound, nonfluorescing state is assigned as $C^2\Delta$. We used depletion spectra of ^{11}BAr and ^{10}BAr to assign the v' vibrational quantum numbers in the $C-X$ transition and find that the binding energy of the $C^2\Delta$ state is $\sim 3,500$ cm^{-1}. We were able to obtain fluorescence depletion spectra of ^{11}BAr and ^{10}BAr separately because

6

of the large isotope splitting in the BAr $B^2\Sigma^+ - X^2\Pi$ electronic spectrum,[12] which was employed as the probe transition. Our observations imply that the BAr($C^2\Delta$) state decays nonradiatively, probably through predissociation.

With depletion spectroscopy, we have been able to observe excitation of the B···H$_2$ complex in this wavelength range. In contrast to the $3s \leftarrow 2p$, free $\leftarrow$ bound transition of B···H$_2$, which is structureless and occurs to the blue of the B atomic $2s2p^2\,{}^2D \leftarrow 2s^22p\,{}^2P$ line, this transition extends to both the red and blue of the atomic transition and does exhibit some low-resolution structure. It is quite likely that the excited B···H$_2$ does not fluoresce since a reaction may occur in the excited state, to yield BH product. We searched, unsuccessfully, for BH $A \rightarrow X$ chemiluminescence, which would signify formation of electronically excited BH($A^1\Pi$) product. Further experiments are continuing, both to observe the corresponding fluorescence depletion spectrum of the B···D$_2$ isotopomer and to probe for BH products from reaction within the excited complex by laser fluorescence detection.

3. Generation of vuv radiation and detection of C atom complexes

In subsequent experiments, we plan to probe the non-bonding interactions of the carbon atom through laser fluorescence excitation spectroscopy of van der Waals complexes. Since the resonance transitions in carbon occur in the vuv (165.7 and 156.0 nm), nonlinear optical generation techniques will be required to prepare the requisite radiation. We constructed a cell containing Hg which can used for frequency tripling[19] of blue light into the vuv. We have also built a glass apparatus for the synthesis[20] of C$_3$O$_2$, which is a suitable photolytic precursor for C atoms. Successful synthesis of C$_3$O$_2$, from the dehydration of malonic acid, has been carried out. We have also acquired a vuv sensitive photomultiplier. Progress on this experiment will depend upon the completion of the fluorescence depletion experiments.

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